Preparation of Long Silver Nanowires from Silver Matrix by Electron Beam Irradiation

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Long silver nanowires with a high aspect ratio of up to 2000 could be obtained from Ag-containing matrix with NASICON structure by electron beam irradiation.

Metallic nanowire whose mechanical and electrical properties differ qualitatively from those of bulk is expected to have applications to electronic and electromechanical devices.[1–3] Since silver has the highest electrical conductivity among all the elements in nature, its nanowire is an especially promising material. Silver nanowires have been prepared using templates such as mesoporous silica[4] and carbon nanotubes,[5] by a wet chemical method[6] or by irradiation of fluorescent light.[7] From the template method, silver nanowires having uniform diameters are obtained, but their lengths are restricted by the template size to several micrometers. The wet chemical method produces silver nanowires with relatively high aspect ratios of a few hundred, but their lengths are less than several micrometers.[6] Electron irradiation of a silver containing matrix is a promising candidate for the preparation of long silver nanowires. However, there has been only a relating report that shows the formation of whisker-like silver by electron beam irradiation.[8] In this work, we succeeded in preparing long silver nanowires with a markedly high aspect ratio using Ag^+-exchanged inorganic ion-exchanger by controlling the irradiation condition.

A silver matrix was prepared by a Ag^+/H^+ exchange reaction of protonated NASICON powder. The NASICON powder (theoretical chemical formula $Na_{2.5}Zr_2Si_{1.5}P_{1.5}O_{12}$) was prepared by a heating method similar to those in the literature.[9,10] Both aqueous solutions of $ZrOCl_2{\cdot}8H_2O$ (1142.8 g) and a mixed solution of $Na_2O{\cdot}3SiO_2$ (298.1 g) and NaOH (95.9 g) were added dropwise simultaneously to $Na_2HPO_4{\cdot}12H_2O$ (204.4 g) aqueous solution while maintaining the pH of the solution at 9.0 with an NaOH solution. The precipitate obtained was filtered, washed with distilled water and then air dried at 80 °C. The NASICON material was prepared by heating the precipitate in air at 1200 °C. The NASICON (3 g) obtained was then treated with a 3 M HCl solution (1000 ml) for 3 h to produce a protonated type. The protonated material was treated with a 0.1 M $AgNO_3$ solution (300 ml) for 3 h, washed with distilled water, and air dried at 80 °C. The final product obtained has a chemical formula of $Ag_{2.3}Na_{0.2}Zr_2Si_{1.5}P_{1.5}O_{12}$ (silver content 30 wt%).

The preparation of silver nanowire was investigated by transmission electron microscopy (TEM JEOL Ltd., JEM-3010) and scanning electron microscopy (SEM, JEOL Ltd., JSM-890) after the powdered samples were dispersed on grids of porous plastic film. The chemical composition of a selected area was examined using energy dispersive X-ray spectroscopy (EDS, Nolan Inst., Vantage) attached to the TEM. The EDS analysis was carried out using a convergent electron probe of 25 nm in diameter.

A typical transmission electron micrograph taken after electron beam irradiation for ca. 25 min under 6.8×10^{-12} A/μm^2 (4.2×10^7 electrons/$\mu m^2{\cdot}s$) at an accelerating voltage of 300 kV is shown in Figure 1. We can see a remarkably long nanowire spun from the matrix and nanoparticles located on the surface of the powder. The nanowire grew slowly like a spider spinning a thread and a long nanowire of ca. 26 nm in diameter and 46 μm in length on the micrograph was finally obtained. The chemical composition of different nanowire parts; A (the original particle), B (the base of the nanowire) and C (the tip of the nanowire), as well as a nanoparticle, were examined by EDS, as is shown in Table 1. The EDS analysis and a selected area electron diffraction (SAED) pattern in a part of the nanowire indicated that the nanowire was a silver metallic crystal with a face-centered cubic structure. The nanowire can therefore be identified as a crystalline silver metallic nanowire, and since silver is monovalent in the original particle, the reaction can be simply written as,

$$Ag^+ + e \rightarrow Ag^0$$

where *e* indicates an electron. Since the silver nanowire is bent not only parallel to the image plane but also perpendicularly, its actual length is estimated to be at least 52 μm based on observations made from different directions of the wire. Thus,

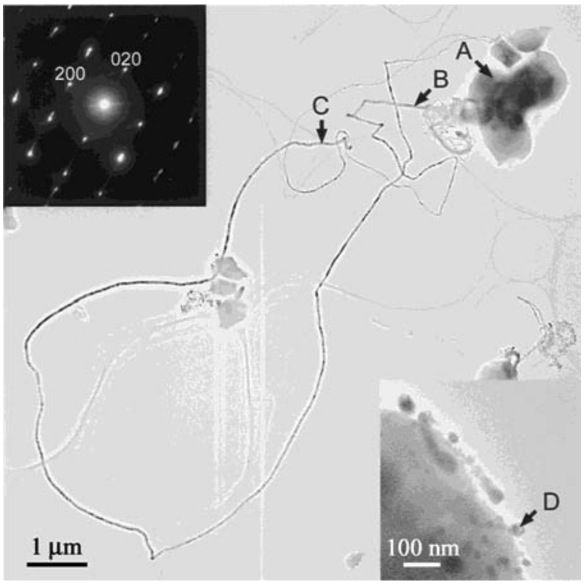

Figure 1. TEM micrograph of a matrix, nanowires and nanoparticles. The nanowires and nanoparticles were produced by electron beam irradiation at 300 kV for ca. 25 min. Inset (top left) is an SAED pattern of part of the nanowire. Inset (bottom right) is a magnified image of the matrix. Components of different parts (A–D) are shown in Table 1.

Table 1. Results of the EDS analysis on different parts (A–D) in Figure 1

	A	B	C	D
Ag	0.99	98.24	99.48	94.72
Na	0.00	0.00	0.00	0.00
Zr	39.00	0.00	0.52	2.10
Si	31.65	1.56	0.00	0.86
P	28.36	0.20	0.00	2.32

Unit: atom%

The results give the amount of atoms of all kinds excluding oxygen in the starting material as 100 atom percent. The EDS analysis was carried out using a convergent electron probe of 25 nm diameter.

the aspect ratio of the wire reaches more than 2000, which is, to our knowledge, the highest among the nano-order silver wires reported to date.

The particles after the electron beam irradiation contain little elemental silver. The nanowire spinning proceeds steadily until the silver element in the matrix is depleted. This suggests that the electron beam irradiation on the matrix produces a strong force that expels metallic silver from the matrix. The nanoparticles, typically 5–40 nm in size, were not observed at the beginning of irradiation, but were observed toward the end of spinning. The nanoparticle arrowed D in Figure 1 consists almost entirely of silver, as does the nanowire (Table 1).

Silver nanowire spinning was recognized at different accelerating voltages of 5, 10, 20, 30, 200 and 300 kV independent of the accelerating voltage. Two kinds of silver nanowire, a clump of nanowires and a linear nanowire, were typically observed as is shown in Figure 2. The very fine clump-type nanowire of 5–15 nm in diameter appeared when it spun vigorously outside the matrix (Figure 2a–c). The thicker linear type nanowire, however, was revealed when it elongated slowly from the surface (Figure 2d–f). The spinning-volume rates estimated from in situ SEM observation were nearly equal (8×10^4 and 3×10^5 nm^3/s, respectively) independent of wire diameter. The diameters of both types of silver nanowires are markedly larger than the bottleneck size (around 0.26 nm) of the Ag^+ ion channels in the NASICON matrix. The nanowire may thicker at the surface of the powder with extremely fine silver lines in the channels bundling together.

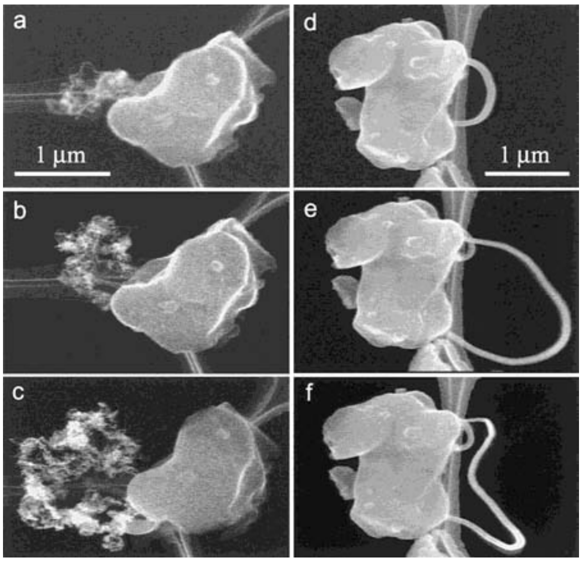

Figure 2. In situ SEM observations of a clump of nanowire (a–c) and a thicker linear nanowire (d–f). Irradiation times of a, b and c are 14, 40 and 392 s, respectively. Irradiation times of d, e and f are 42, 76 and 78 s, respectively.

TEM observation showed that the nanowire spinning was more vigorous when the sample was irradiated by a convergent electron beam. This result suggests that the rate of nanowire spinning depends mainly on the current density of the irradiating electron beam, and not on the accelerating voltage. At a high current density, since the nanowire spinning progresses vigorously from the matrix, the nanowires are liable to bend away from a straight line. They often bend markedly to abut on the surface of the powder. On the other hand, the nanowire tends to elongate slowly with less bending at a relatively low current density. Thus, a low current density is advantageous for the formation of long silver nanowire.

The silver content of the original powder is an important factor controlling the spinning of silver nanowire. In a matrix with smaller silver content (chemical composition $Ag_{0.5}H_{1.8}Na_{0.2}Zr_2Si_{1.5}P_{1.5}O_{12}$, silver content 10 wt%), a TEM photograph after electron beam irradiation did not show any nanowires, but only nanoparticles, similar to those in Figure 1, observable on the surface of the matrix. This result suggests that electron beam irradiation generates sufficient force to expel elemental silver from the matrix regardless of silver content, but there is a minimum threshold of silver content that enables the formation of nanowire.

Silver nanowire spinning was not recognized in some kinds of powders, Ag^+-exchanged cubic antimonic acid (high Ag^+ selectivity), hollandite type manganese oxide (with 2 × 2 tunnel) and zeolite (type A), despite their Ag^+ contents being markedly high (above 10 wt%). In addition to the silver content, easy migration of Ag^+ ions from inside to the surface of the powder may be necessary for the formation of nanowire. Silver atoms must be supplied smoothly to ion channel outlets of the powder for the formation of silver nanowire. Materials with a NASICON structure may be well suited for precursor to spin silver nanowire, since they are generally good ionic conductors due to the presence of channels through which Ag^+ ions can move easily.[11–13]

References

1 H. Ohnishi, Y. Kondo, and K. Takayanagi, *Nature*, **395**, 780 (1998).
2 A. I. Yanson, G. R. Bollinger, H. E. van den Brom, N. Agraït, and J. M. van Ruitenbeek, *Nature*, **395**, 783 (1998).
3 Y. Kondo and K. Takayanagi, *Science*, **289**, 606 (2000).
4 M. H. Huang, A. Choudrey, and P. Yang, *Chem. Commun.*, **2000**, 1063.
5 J. Sloan, D. M. Wright, H. Woo, S. Bailey, G. Brown, A. P. E. York, K. S. Coleman, J. L. Hutchison, and M. L. H. Green, *Chem. Commun.*, **1999**, 699.
6 N. R. Jana, L. Gearheart, and C. J. Murphy, *Chem. Commun.*, **2001**, 617.
7 S. Liu, J. Yue, T. Cai, and K. L. Anderson, *J. Colloid Interface Sci.*, **225**, 254 (2000).
8 C. Fan and G. Meng, *J. China Uni. Sci. Tech.* (in Chinese), **18**(1), 139 (1988).
9 A. Ono, *J. Mater. Sci.*, **19**, 2691 (1984).
10 Y. Shimizu, Y. Azuma, and S. Michishita, *J. Mater. Chem.*, **7**(8), 1487 (1997).
11 H. Y. Hong, *Mater. Res. Bull.*, **11**, 173 (1976).
12 J. B. Goodenough, H. Y. Hong, and J. A. Kafalas, *Mater. Res. Bull.*, **11**, 203 (1976).
13 A. Martínez-Juárez, C. Pecharromán, J. E. Iglesias, and J. M. Rojo, *J. Phys. Chem.*, **B102**, 372 (1998).